"STUDIES ON INFLUENCE OF SYNTHESIS PARAMETERS ON THE PROPERTIES OF SPINEL FERRITES PREPARED BY WET CHEMICAL METHOD"

A Synopsis Submitted to

Dr. Babasaheb Ambedkar Marathwada University,
Aurangabad

For the Degree of

Doctor of Philosophy

In

Physics

By

Rekha Ramrao Parlikar

Under the Guidance of

Dr. K. M. Jadhav
Senior Professor,
Department of Physics,
Dr. Babasaheb Ambedkar Marathwada University, Aurangabad

June-2022

Final Synopsis

"STUDIES ON INFLUENCE OF SYNTHESIS PARAMETERS ON THE PROPERTIES OF SPINEL FERRITES PREPARED BY WET CHEMICAL METHOD"

Introduction

Magnetic oxide systems like ferrite with ferrimagnetic nature are of current interest to many researchers. Ferrites consist of iron oxide (Fe_2O_3) and metal oxide (MO) as their main constituents [1]. They possess very good electrical and magnetic properties which can be varied to suit for the desired applications. Many researchers have investigated their structural, electrical, optical and magnetic properties using standard techniques by substituting various cations and varying preparation techniques [2]. On the basis of crystal structure ferrite are grouped into three types namely spinel ferrite, rare earth garnet and hexagonal ferrites [3]. Spinel ferrite have the chemical formula MFe_2O_4 (M = Co, Zn, Ni etc.) and possess cubic structure with two interstitial sites namely tetrahedral (A0 and octahedral [B] site [4]. Spinel ferrites are more attractive than other ferrites because of their excellent electrical and magnetic properties which are sensitive to various parameters [5]. Large numbers of researchers have investigated various electrical and magnetic properties of spinel ferrite because of their excellent electrical properties such as DC resistivity, activation energy, drift mobility, low eddy current and dielectric losses etc and magnetic properties such as saturation magnetization, permeability, magnetocrystalline anisotropy etc [6]. These properties of spinel ferrite have made them useful in many industrial and domestic applications like antenna rod, transformer core, sensors, catalyst, high frequency devices etc. Recently, from last two decades spinel ferrite in nanocrystalline form have shown very good properties which are better than the properties exhibited by bulk spinel ferrites.

The nanosize of the particles, large surface to volume ratio, greater homogeneity, high stability, easy preparation with large yield, greater reactivity at atomic/ molecular level are the characteristics features of spinel ferrite in nanocrystalline form [7]. To prepare spinel ferrite in nanocrystalline form, top down and bottom up approach o the nanotechnology are useful. Chemical co-precipitation, sol-gel, hydrothermal etc are the important and commonly used wet chemical methods. Many researchers have investigated the structural, morphological, optical, magnetic properties of various nanocrystalline spinel ferrites in pure and substituted form. These nanoparticles of spinel ferrite have very good applications in the field of medical science and environment for water purification, sensors, catalyst, magnetic data storage photocatalytic degradation of organic dyes [8]. Therefore, the processing and their characterization using variety of ways are of great interest to many researchers. The method of preparation plays vital role in the modification of properties of the ferrite materials. Currently, to avoid the toxic gases and use of hazardous chemicals, green synthesis approach has been emerged [9]. Further, the pH, metal nitrate ratio, annealing temperature etc also plays crucial role in the modification of properties of spinel ferrite materials. In the family of spinel ferrite cobalt ferrite is very much promising candidate having very good dielectric, electrical, optical, magnetic and other properties. Many researchers have investigated these properties of cobalt ferrite in nanocrystalline form for various applications. Mixed spinel ferrite like cobalt cadmium ($Co_{0.7}Cd_{0.3}Fe_2O_4$) shows very good magnetic and electrical properties. In view of this, in the present studies the mixed spinel ferrite $Co_{0.7}Cd_{0.3}Fe_2O_4$ has been synthesized by using sol-gel autocombustion method assisted by 1. organic fuel like dextrose 2. Biogenic fuel/ green fuel like black pepper to understand the role of fuel. The synthesis of $Co_{0.7}Cd_{0.3}Fe_2O_4$ was carried out by varying the metal nitrate to fuel

ratio. The structural, morphological, electrical, dielectric magnetic and optical properties of the $Co_{0.7}Cd_{0.3}Fe_2O_4$ spinel ferrite were investigated in the light of varying fuel and varying metal nitrate to fuel ratio. The results of these studies are presented in this work.

Literature Survey

Sumithra Y Srinivasan et al [8] synthesized metal-substituted cobalt ferrites [$M_xCo_{(1-x)}Fe_2O_4$ (M = Zn, Cu, Mn; x = 0.0, 0.25, 0.5, and 0.75)] via a sol–gel technique. The ferrite structures were confirmed by X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, surface analysis using the Brunauer–Emmett–Teller method, and energy-dispersive X-ray spectroscopy and also examined the antimicrobial activity of these ferrites against selected pathogenic microbes.

V.R.Bhagwat et al [10] successfully synthesized spinel structured cobalt ferrite ($CoFe_2O_4$) nanoparticles by sol-gel auto combustion method using three different fuels (Ethylene glycol, Glycine and Urea) approach. The author reported that using urea as a fuel one can obtain smaller particle size while the improved magnetic properties were observed for ethylene glycol as a fuel.

Devi A. Gole et al [11] prepared cobalt ferrite ($CoFe_2O_4$) by co-precipitation method and carried out its subsequent characterization by using X-ray diffraction (XRD), atomic force microscope (AFM), TG-DTA and Fourier transform infrared spectroscopy (FTIR) techniques. The influence of pH variation on structural properties of cobalt ferrite nanoparticles was also investigated by the author.

P.Annie Vinosha and S.Jerome Das [12] Investigated the role of pH on the structural, optical and magnetic properties of cobalt ferrite nanoparticles and its effect on the photo-fenton activity.

B. Jansi Rani et al [13] synthesized ferrimagnetic cobalt ferrite ($CoFe_2O_4$) nanoparticles by employing co-precipitation method and investigated physicochemical and magnetic properties with respect to cetyl trimethylammonium bromide (CTAB), hexamethylenetetramine (HMT) and polyethylene glycol (PEG-400) surfactants.

İbrahim Hakkı Karakas [14] studied the effects of fuel type onto the structural, morphological, magnetic and photocatalytic properties of nanoparticles in the synthesis of cobalt ferrite nanoparticles with microwave assisted combustion method.

P. Annie Vinosha et al [15] investigated the impact of nickel substituted cobalt ferrite nanocrystals, which were synthesized by a facile co-precipitation technique. The various physical properties such as structural, electrical, magneto-optical and thermal were studied.

Budi Purnama et al [16] studied the effect of calcination temperature on structural and magnetic properties in cobalt ferrite nano particles.

Aim of the proposed work

The aim of the present work is to prepare cobalt/ nickels based spinel ferrite nanoparticles with cadmium doping using organic fuel/ green fuel assisted sol-gel auto combustion technique. To understand the role of metal nitrate to fuel ratio Cd doped cobalt ferrite was prepared by varying fuel ratio. The structural, morphological, electrical and dielectric properties were investigated using standard techniques such as X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, vibrating sample magnetometer, two probe technique and LCR-Q meter.

Experimental details:

Synthesis of Cd doped cobalt ferrite ($Co_{0.7}Cd_{0.7}Fe_2O_4$) using dextrose assisted sol-gel auto-combustion synthesis

Materials

Cobalt nitrate (Co $(NO_3)_2 \cdot 6H_2O$), cadmium nitrate ($Cd(NO_3)_2$), ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$), dextrose ($C_6H_{12}O_6$), ammonia solution (NH_3), acetone (C_3H_6O), distilled water were obtained from SD Fine chemicals. All chemical used were of analytical grade and the solutions were prepared with distilled water.

Sample Preparation Method

The preparation of cobalt ferrite nanoparticles by using two different inorganic fuels i.e. dextrose as a chelating agent was carried out by employing simple as well as cost effective sol-gel auto-combustion method. Stoichiometric amounts of said chemicals were added into distilled water and pH of the solution was adjusted to 7 using ammonia solution. The solution heated at ~90°C on the hot plate with constant stirring at 500 rotations per minute for 2 h. After the formation of viscous gel temperature was raised up to 110-120°C. The ignition of the dried gel takes place and finally it gives ash. This burnt ash is a grind by using mortar and piston to obtain fine Ni-Zn Spinel Ferrite Nanoparticles. The obtained powder was sintered at 600°C for 4h to remove impurities added during synthesis. The obtained nanopowder was used for the further characterizations like X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, vibrating sample magnetometer etc.

Characterization Tools

The structural characterizations of the all the prepared nanoparticles were carried out by Bruker D8 advance X-ray diffractometer with copper target. Measurements were recorded at room temperature.

The Fourier transform infrared spectroscopy (FTIR) studies were carried out with help of a Perkin-Elmer spectrophotometer. Raman spectroscopy was used to carry out micro-structural analysis.

The morphological investigation of the prepared nanoparticles sample was carried out using field emission scanning electron microscopy (FE-SEM) and field emission transmission electron microscopy technique (FE-TEM).

The vibrating sample magnetometer was employed to investigate the magnetic properties of all the samples at room temperature.

The dielectric properties of the present sample were studied by LCR-Q meter in the frequency range of 100Hz to 1MHz at room temperature.

Results and discussion

The X-ray diffraction pattern recorded at room temperature of $Co_{0.7}Cd_{0.3}Fe_2O_4$ prepared by dextrose assisted sol-gel autocombustion method is shown in fig. 1. below. The study of X-ray diffraction pattern using Powder X software show the formation of single phase cubic spinel structure. All the reflections seen in the XRD pattern belongs to cubic structure. All these reflections are indexed using Bragg's law.

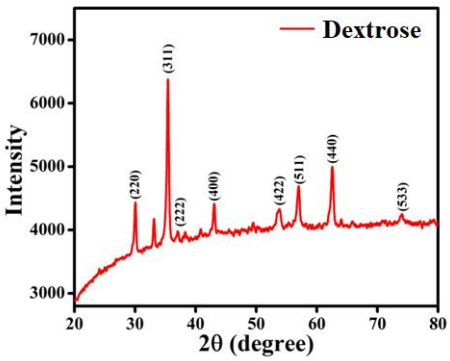

Fig. 1 XRD pattern of dextrose assited $Co_{0.7}Cd_{0.3}Fe_2O_4$ nanoparticles

The XRD data such as interplanar spacing‘d’, Bragg’s angle etc was utilized to calculate lattice constant and other structural parameters. The observed lattice constant was found to be less than pure cobalt ferrite indicating successful incorporation of Cd ions. The results of lattice constant and other structural parameters such as unit cell volume, X-ray density etc are in good agreement with the reported values. The crystallite size was determined from the Debye Scherrer equation and by using the full width at half maxima of the highest intensity peaks (311) present in the XRD pattern.

Fig. 2 depicts FTIR spectrum of the prepared nanoparticles.

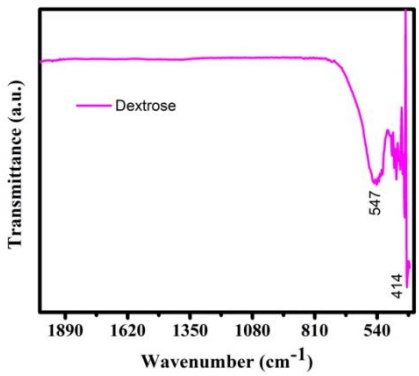

Fig. 2 FTIR spectrum of $Co_{0.7}Cd_{0.3}Fe_2O_4$ nanoparticles

The nanoparticles of $Co_{0.7}Cd_{0.3}Fe_2O_4$ were also chacterized by means of Fourier trnasform inrared spectroscopy technique. The spectrum show two absorption bands near 400cm^{-1} and 600 cm^{-1} charcteizing the spinel struuctre. These absorption bands were used to find out force constnant and other paramters.

Field emmison scanning electron microscopy (FE-SEM) was used to study the surface morphology of the prepared nanoparticles. FE-SEM iamges of the prepared sample show very fine grains more or less spherical in nature.

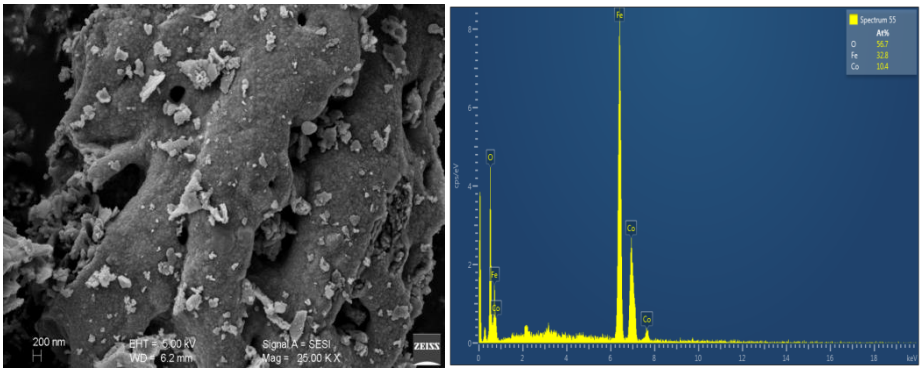

Fig. 3 FESEM image and EDS spectra of dextrose assisted $Co_{0.7}Cd_{0.3}Fe_2O_4$ nanoparticle

The grain size was determined using the linear intercept method which is obtained to be 34 nm. The elelmetnal analysis was performed using EDS spectrum which show the presence of Co, Cd, Fe and O ions. All these elements are according to the stoichiometric proportion.

The dielctric properties such as dielctric cosntat, dielectric loss and dielctric loss tangent were investiagted using LCR-Q meter. The capcitance C was measured for varying frequency and at room temperature. The dielectric constant was obtianed using the standard relation and there variation with frequency is shown in Fig. 4. It is observed from Fig. 4 (a) that as frequency increases from 50Hz to 1MHz the dielctric constant goes on decresing. The decrease in dielctric cosntant at low frequency is very fast as comaprd to the decrease in dielctric constnat at high frequuecny. This

behaviour of the dielctric constnat is similler to that reported in the literature. The obsreved dielctric dispersion is exaplined on the basis of Maxwell's Wagner theory.

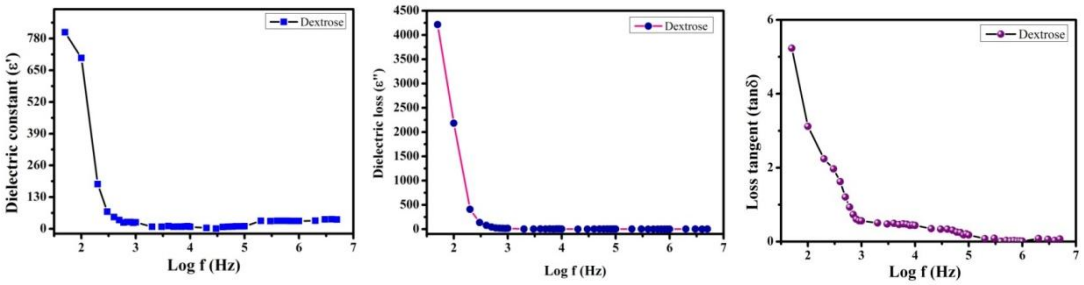

Fig. 4 Variation of (a) dielectric constant (b) dielectric loss and (c) dielectric loss tangent with frequency

The variation of dielectric loss as a function of frequency is shown in Fig. 4. (b). It is observed from Fig. 4 (b) that the dielectric loss is also decreases with increase in frequency and obeys exponential law.

The dielectric loss tangent was also calculated from the known values of dielectric constant and dielectric loss taking their ratio. The dependence of dielectric loss tangent on the frequency is depicted in Fig. 4 (c). The variation dielectric loss tangent with frequency also exhibit similar behaviour to that of dielectric constant, dielectric loss and dielectric loss tangent. It is noted from Fig. 4(c) that at low frequency regions the dielectric loss tangent show highest values. As frequency increase the dielectric loss tangent goes on decreasing slowly. The dielectric loss tangent almost remains same and higher frequency. This behaviour of dielectric loss tangent with frequency is also explained using the Maxwell –Wagner theory.

The important magnetic properties were studied at room temperature using vibrating sample magnetometer technique. The plot of magnetization M against applied field H is shown in Fig. 5, which exhibits normal ferrimagnetic behaviour. The values of

saturation magnetization, coercivity, remanence magnetization are obtained from M-H hysteresis curve. It is observed that the saturation magnetization slightly increases as compared to pure cobalt ferrite. The increase in saturation magnetization may be due to the cadmium ion, which occupy the tetrahedral (A) site. The observed behaviour magnetization can explained on the basis of Neel's model.

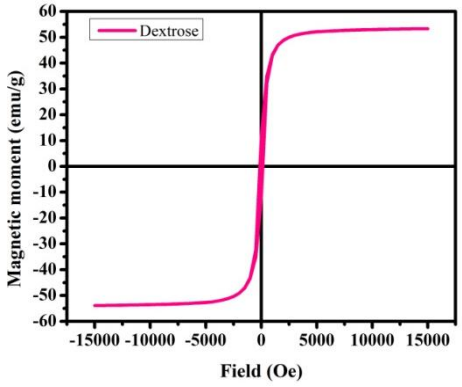

Fig. 5 M-H hysteresis loop of $Co_{0.7}Cd_{0.7}Fe_2O_4$ nanoparticles prepared by dextrose assisted sol-gel auto-combustion synthesis

Synthesis of Cd doped cobalt ferrite ($Co_{0.7}Cd_{0.7}Fe_2O_4$) using black pepper (Green Fuel) assisted sol-gel auto-combustion synthesis

Materials

The synthesis of cobalt ferrite nanoparticles was prepared by suing cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$), ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$), cadmium nitrate ($Cd(NO_3)_2$) as a precursor. The biogenic fuels such as black pepper (Piper nigrum) was used a as chelating agent. Ammonia solution (NH_3), acetone (C_3H_6O) and distilled water were obtained from Fisher Scientific PVT limited. All chemical used were of analytical grade and the solutions were prepared with distilled water.

Sample Preparation

The $CoFe_2O_4$ spinel ferrite samples were prepared by the sol–gel auto-combustion technique. Black pepper (Piper nigrum) was used as fuel to avoid toxic gases produces during combustion process. Stoichiometric proportion of metal nitrates was added in a minimum amount of deionized water to form homogeneous solution. The mixed nitrate solution was stirred well with a drop by drop liquid ammonium hydroxide (NH_4OH) to maintain the pH value at 7. Mixed solution was simultaneously heated at 70 °C for 3 h to form a sol. Transparent sol was heated at 110 °C for 1 h for the removal of water. With the increase in a temperature sol turns in viscous brown gel. Under constant stirring and heating, viscous brown gel transform into dried gel. The autocatalytic nature of the combustion process of nitrate-fuel gel was studied and the experimental observations showed that the dried gel formed from metal nitrates and biogenic fuel exhibited self-propagating combustion behavior, and the entire combustion process was done in few minutes. At a proper temperature ignition started and the dried gel burnt in a self propagating combustion manner until all the gel was burnt out completely to form a fluffy loose powder of cobalt ferrite. The obtained powder was sintered at 600°C for 4h to remove impurities added during synthesis.

Characterizations tools

The X-ray diffractometer (Bruker D8 advance) was employed for the investigation of structural characterizations of the all the prepared nanoparticles Measurements were recorded at room temperature. The Fourier transform infrared spectroscopy (FTIR) studies were carried out with help of a Perkin-Elmer spectrophotometer. Raman spectroscopy was used to carry out micro-structural analysis. The microstructure and

surface morphology of the prepared nanoparticles sample was carried out using field emission scanning electron microscopy (FE-SEM). The vibrating sample magnetometer was employed to investigate the magnetic properties of all the samples at room temperature. The dielectric properties of the present sample were studied by LCR-Q meter in the frequency range of 100Hz to 1MHz at room temperature.

Results and discussion

X-ray diffraction pattern of $Co_{0.7}Cd_{0.3}Fe_2O_4$ nanoparticle prepared by using black pepper (green fuel) is presented in Fig. 6. From Fig. 6 it is observed that all the reflections belong to cubic structure. The XRD pattern of the present sample reveals the single phase cubic spinel structure. There is no other extra peak observed in the XRD pattern which confirms the purity of the sample. The lattice constant, crystallite size, X-ray density etc structural parameters were calculated by using the interplanar spacing, Bragg's angle, FWHM. The crystallite size obtained was of the order of few nanometers.

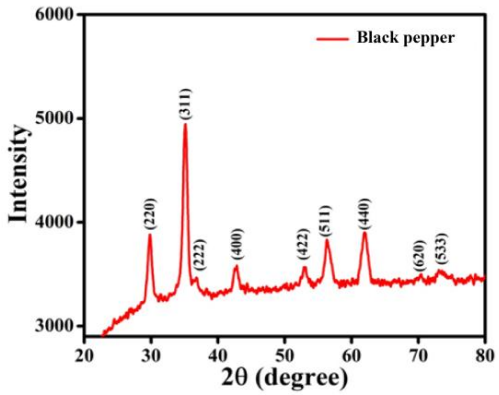

Fig. 6 XRD pattern of $Co_{0.7}Cd_{0.3}Fe_2O_4$ nanoparticle

The Fourier transform infrared spectroscopy (FTIR) of black peeper assisted $Co_{0.7}Cd_{0.3}Fe_2O_4$ nanoparticle is depicted in Fig. 7. The FTIR spectrum reveals two main peaks observed near 550 cm^{-1} and 400 cm^{-1}. In ferrites, the band appearing at the

higher wave number (500–600 cm^{-1}) is assigned to the tetrahedral complexes, while the band appearing at lower wave number (400–450 cm^{-1}) is assigned to the octahedral complexes.

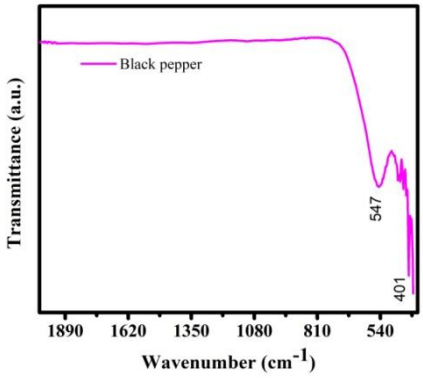

Fig. 7 FTIR spectrum of $Co_{0.7}Cd_{0.3}Fe_2O_4$ nanoparticle

The field emission scanning electron was used to investigate the surface morphology of the black pepper assisted. The FE-SEM micrographs of $Co_{0.7}Cd_{0.3}Fe_2O_4$ nanoparticle is depicted in the Fig. 8. The FE-SEM micrographs show spherical grains with slight agglomeration. The elemental composition was verified through energy dispersive spectroscopy (EDS) analysis. The EDS spectrum reveals the presence of Co, Cd, Fe and O ions in proper proportion. The values of atomic percentage confirms that the prepared sample maintain the stoichiometric proportion.

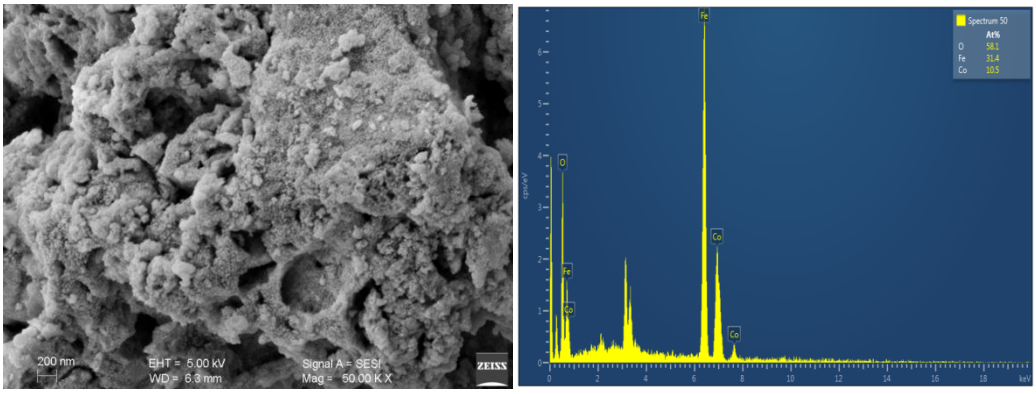

Fig. 8 FESEM image and EDS spectra of Black pepper assisted $Co_{0.7}Cd_{0.3}Fe_2O_4$ nanoparticle

The magnetic properties of the prepared samples were measured by using vibrating sample magnetometer (VSM). Fig. 9 represents the M-H hysteresis loop. The M-H hysteresis loop reveals the normal ferrimagnetic behaviour.

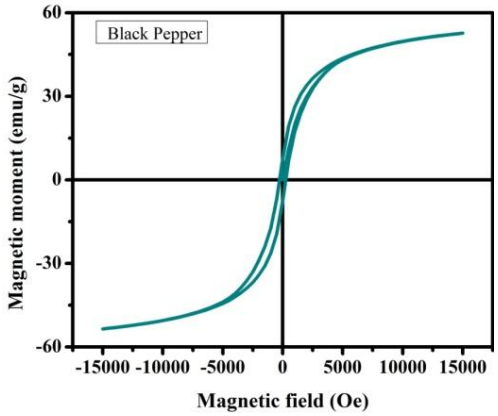

Fig. 9 M-H hysteresis loop of $Co_{0.7}Cd_{0.3}Fe_2O_4$ nanoparticle

The M-H hysteresis curve was used to calculate the saturation magnetization, coercivity and remanence magnetization. The low values of coercivity indicate the superparamagnetic behaviour of the samples. The observed behaviour magnetization can explained on the basis of Neel's model.

The variation in of dielectric constant, dielectric loss, and dielectric loss tangent against frequency for $Co_{0.7}Cd_{0.3}Fe_2O_4$ nanoparticle is shown in Figure 10 (a), (b) and (c). The dielectric constant of the Cd doped cobalt ferrite ($Co_{0.7}Cd_{0.3}Fe_2O_4$) decreases with the increase in the frequency.

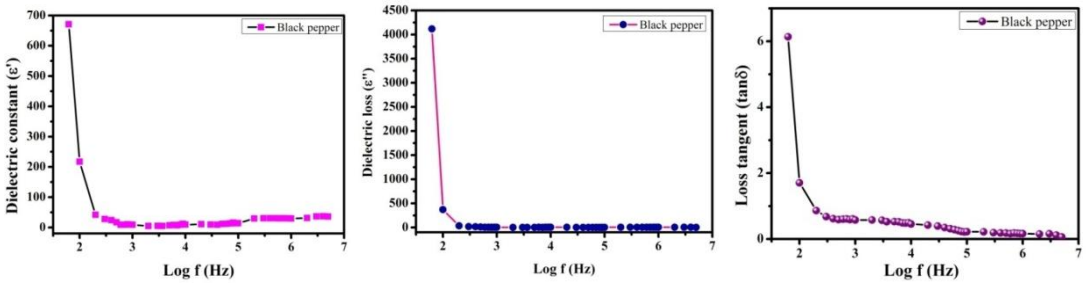

Fig. 10 Variation of (a) dielectric constant (b) dielectric loss and (c) dielectric loss tangent with frequency

It is observed from Fig. 10 that all the dielectric parameters get decreased with increase in frequency in exponential manner. The observed dielectric behaviour can be explained on the basis of Maxwell-Wagner theory.

Synthesis of Cd doped cobalt ferrite ($Co_{0.7}Cd_{0.7}Fe_2O_4$) nanoparticles by dextrose assisted sol-gel autocombustion method : Effect of varying metal nitrate to fuel ratio.

Materials

The high purity cobalt nitrate [$Co(NO_3)_2$ H_2O], cadmium nitrate ($Cd(NO_3)_2$), ferric nitrate [$Fe(NO_3)_3 9H_2O$] and dextrose ($C_6H_{12}O_6$) were used as starting material. Ammonia solution was used to adjust the pH. The distilled water was used throughout the experiment. All the chemicals were purchased from Fisher Scientific PVT. limited.

Sample preparation

Cobalt ferrites ($Co_{0.7}Cd_{0.3}Fe_2O_4$) with different metal nitrate to fuel ratios i.e. 1:1.2, 1:1.6, 1:2.0 and 1:2.4 were synthesized by sol–gel auto-ignition method. The stoichiometry amounts of metal nitrates were dissolved in a citric acid aqueous solution. The molar ratio of nitrates to citric acid was taken 1:1.2, 1:1.6, 1:2.0 and 1:2.4. A homogenous transparent solution was obtained after the reaction completed. An appropriate amount of ammonia solution was added to the solution to adjust the pH value about 7. During this process, the solution was continuously stirred using a magnetic agitator. The mixed solution was stirring at 90 C for 1 h. During evaporation, the solution became viscous and finally converted into a very viscous brown gel. Finally all the remaining water was released from the mixture and the sticky mass began to bubble and the gel automatically burnt with glowing flints. The

decomposition reaction continued till the whole citrate complex was consumed. The auto-ignition was completed within five minute, yielding the brown colored ashes termed as precursor. The as-prepared powders of all the samples were heat treated separately at 500 °C for 5h in the muffle furnace to get the final product.

Characterizations tools

The structure of the $Co_{0.7}Cd_{0.3}Fe_2O_4$ nanoparticles was characterized by the X-ray diffraction (XRD) technique using a Bruker D8 advance X-ray diffractometer using (0.15 nm) radiation (operated at 40kV and 200mA). to generate diffraction patterns from the crystalline powder samples at room temperature in the range from 10° to 80°.

The Fourier transform infrared spectroscopy (FTIR) studies were carried out with help of a Perkin-Elmer spectrophotometer.

The morphology of the prepared $Co_{0.7}Cd_{0.3}Fe_2O_4$ nanoparticles was studied by using field emission scanning electron microscopy (FE-SEM).

Magnetic properties of the prepared cobalt ferrite nanoparticles were performed by using a vibrating sample magnetometer (VSM) (Lake Shore 4700). The measurements were recorded in room temperature with a maximum magnetic field of 15kOe.

The dielectric properties of the present sample were studied by LCR-Q meter in the frequency range of 100Hz to 1MHz at room temperature.

Results and discussion

Fig. 11 illustrate the X-ray diffraction pattern of $Co_{0.7}Cd_{0.3}Fe_2O_4$ nanoparticles synthesized using sol-gel autocombustion technique and by varying the metal nitrate to fuel ratio as 1:1.2, 1:1.6, 1:2.0 and 1:2.4.

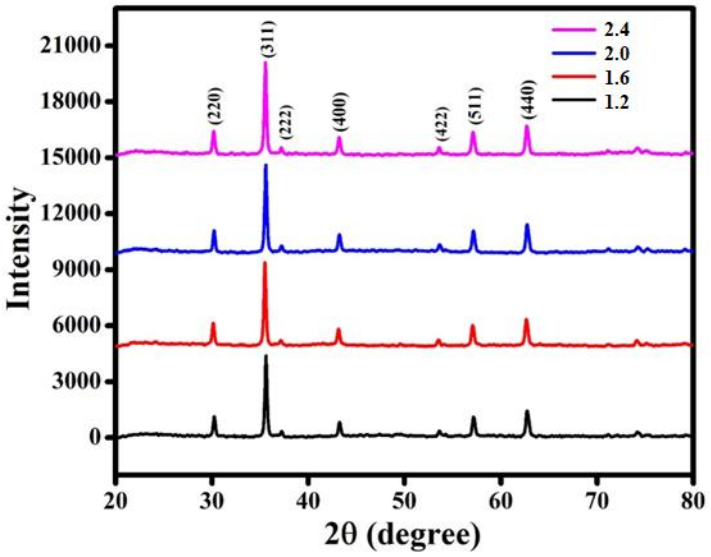

Fig.11. XRD pattern of $Co_{0.7}Cd_{0.3}Fe_2O_4$ nanoparticles for different metal nitrate to fuel ratio

It is clear from Fig. 11 that all the X-ray diffraction pattern show same reflections but with varying intensity and broadening. All the reflections present in the XRD patterns belongs to cubic spinel structure. No extra peak other than cubic phase was observed in the XRD pattern indicating the single phase formation with cubic structure. The crystallite size of all the samples was calculated using Debye Scherrer formula which shows variation in the values may be due to the varying ratio of metal nitrate to fuel. The lattice constant and other structural parameters were also determines which show slight variation in their values.

All the samples were also characterized by Fourier transform infrared spectroscopy techniques. The FTIR spectra is shown in fig. 12, which shows the two prominent absorption bands.

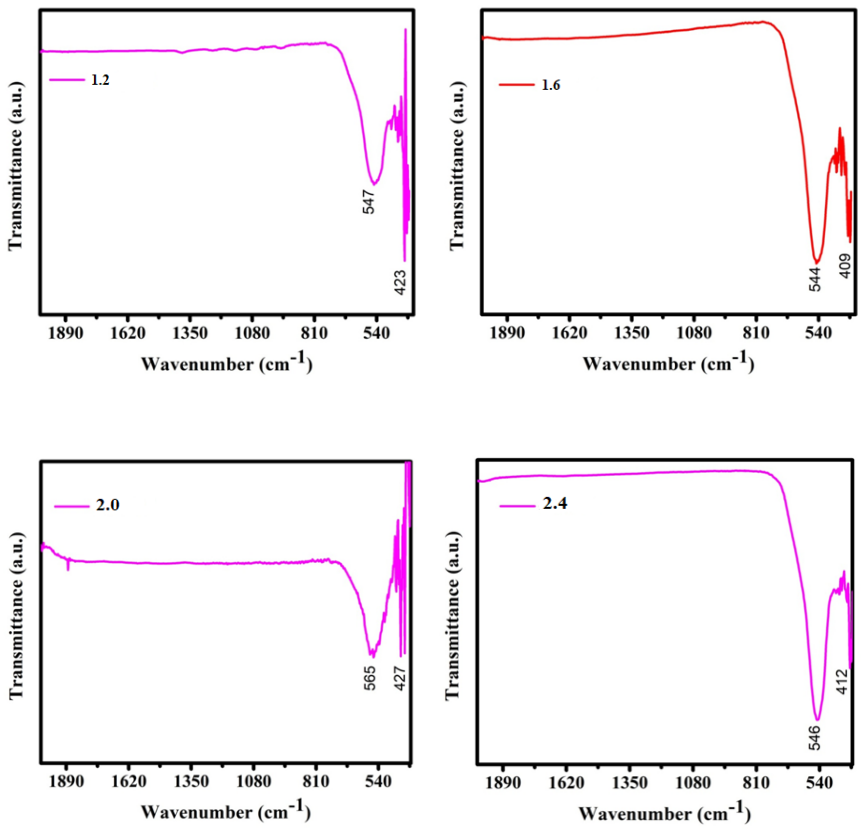

Fig. 12 FTIR spectra of the $Co_{0.7}Cd_{0.3}Fe_2O_4$ nanoparticles for different metal nitrate to fuel ratio

The sample having the ratio 1:1.2, 1:1.6, 1:2.0 and 1:2.4 show the bands at 547 cm^{-1} and 423 cm^{-1}, 544 $cm^{-1}$and 409 cm^{-1}, 565 $cm^{-1}$and 427 cm^{-1}, 546 cm^{-1} and 412 cm^{-1} respectively. The variation observed in the band frequency can be attributed to the varying ratio of metal nitrate to fuel. The observed values were used to determine force constant and other parameters.

The surface morphological aspects of all the samples were studied by means of scanning electron microscopy technique. Fig. 13 (a), (b), (c) and (d) shows field

emission scanning electron microscopy images of all the samples recorded for highest magnification. These images were used to obtained grain size and specific surface area.

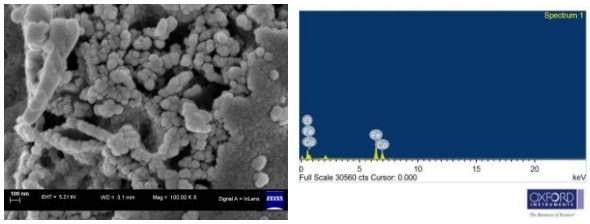

Fig. 13 (a) FE-SEM image and EDS spectra of $Co_{0.7}Cd_{0.3}Fe_2O_4$ NPs (ratio 1:1.2)

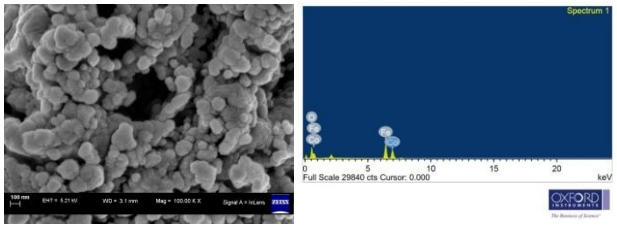

Fig. 13 (b) FE-SEM image and EDS spectra of $Co_{0.7}Cd_{0.3}Fe_2O_4$ NPs (ratio 1:1.6)

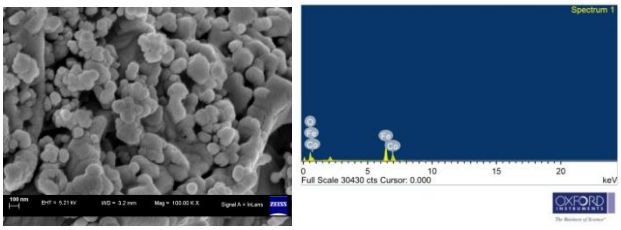

Fig. 13 (c) FE-SEM image and EDS spectra of $Co_{0.7}Cd_{0.3}Fe_2O_4$ NPs (ratio 1:2.0)

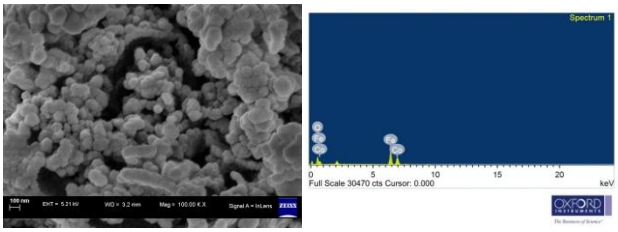

Fig. 13 (d) FE-SEM image and EDS spectra of $Co_{0.7}Cd_{0.3}Fe_2O_4$ NPs (ratio 1:2.4)

The FE-SEM images show the dense structure with slight agglomeration particles. Fig. 13 (a) shows particles with elongated structure grains and also shows some spherical grains. The other images show the presence of spherical particles.

The magnetic properties of all the samples were investigated using vibrating sample magnetometer (VSM) technique. All the samples exhibits typical ferrimagnetic behaviour The M-H plots recorded at room temperature were used to obtain various magnetic parameters. It is noted from the fig.14 that the saturation magnetization

increases with increasing metal nitrate to fuel ratio. The saturation magnetization of the sample having ratios 1: 2.0 and 1: 2.4 are close to each other. The other magnetic parameters also show similar trend.

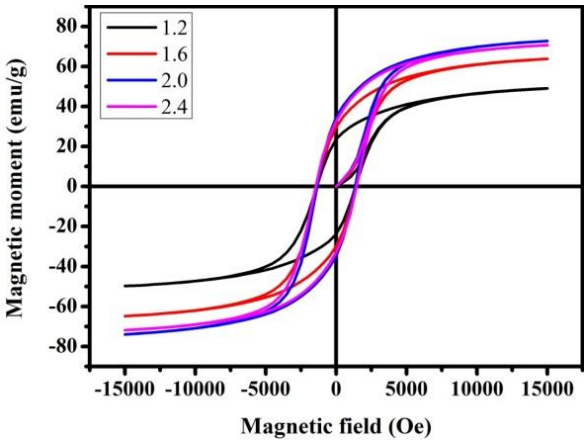

Fig. 14 Magnetization hysteresis loop of $Co_{0.7}Cd_{0.3}Fe_2O_4$ nanoparticles

The dielectric properties of all the samples were investigated by means of LCR-Q meter. The frequency dependence dielectric constant, dielectric loss and dielectric loss tangent recorded at room temperature are shown in fig. 15 (a), (b) and (c) respectively for varying ratio of metal nitrate to fuel.

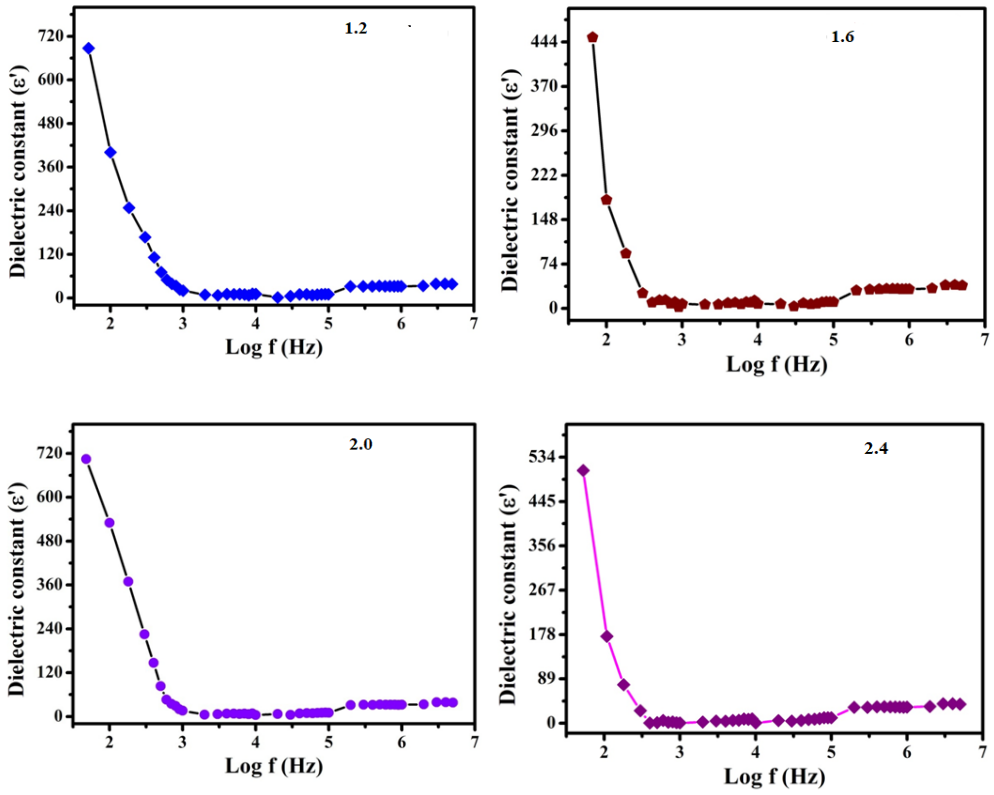

Fig. 15 (a) Variation of dielectric constant $Co_{0.7}Cd_{0.3}Fe_2O_4$ nanoparticles

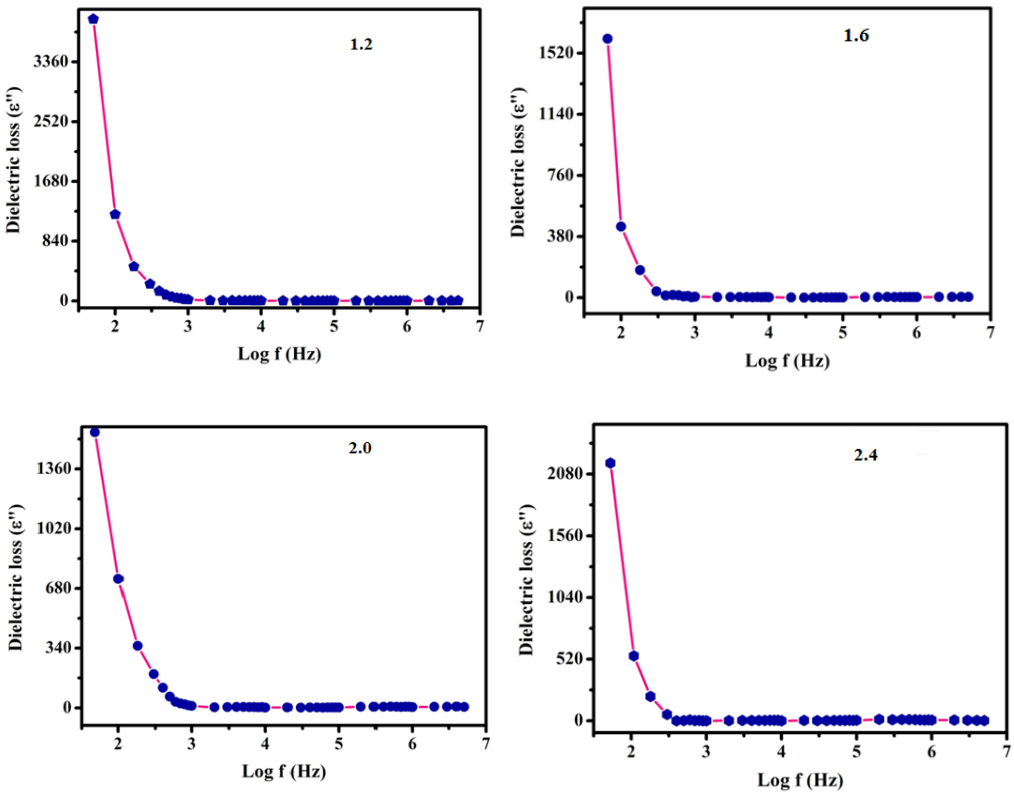

Fig. 15 (b) Variation of dielectric loss $Co_{0.7}Cd_{0.3}Fe_2O_4$ nanoparticles

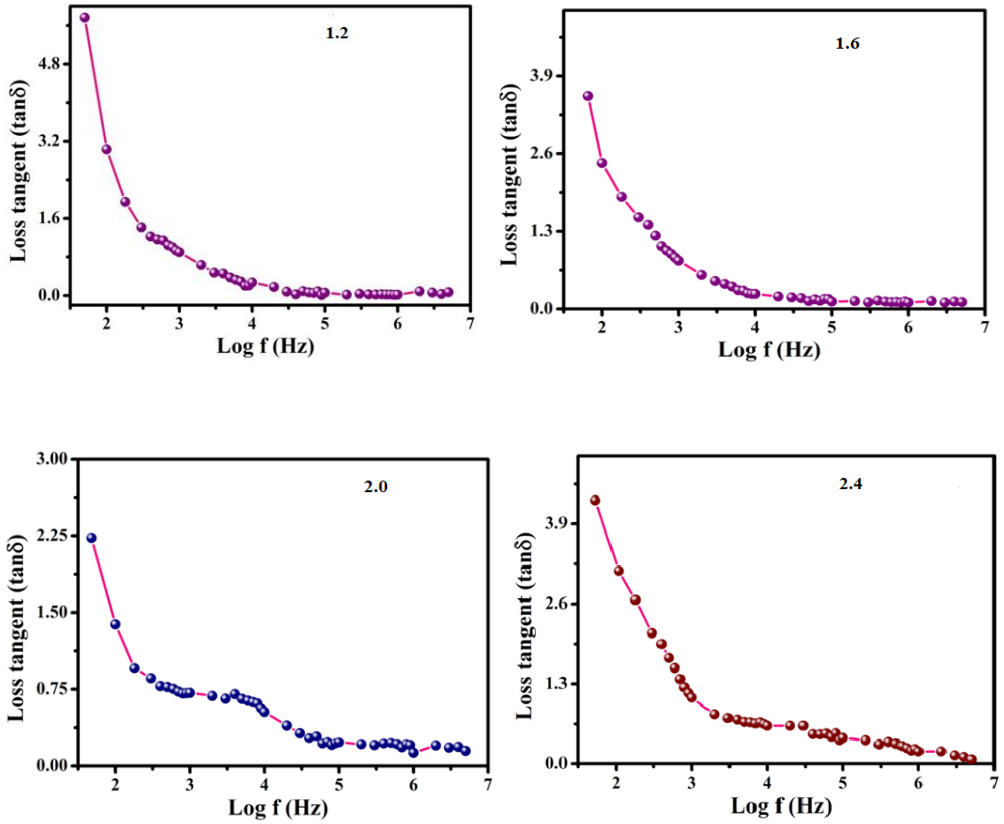

Fig. 15 (c) Variation of dielectric loss tangent $Co_{0.7}Cd_{0.3}Fe_2O_4$ nanoparticles

It is evident from the figures that all the dielectric parameters that is dielectric constant, dielectric loss and dielectric los tangent all get decreases with frequencies. The decrease in dielectric parameters is observed to be in exponential manner. At low frequency dielectric instant is highest and as frequency increases dielectric parameters decrease suddenly. Further increase in frequency does not much affects the values of dielectric parameters. At high frequency the dielectric parameters remains almost same. The dielectric constant, dielectric loss and dielectric loss tangent all show strong dependence of ratio of metal nitrates to fuel.

Conclusions

The samples of $Co_{0.7}Cd_{0.3}Fe_2O_4$ nanoparticles were prepared by different fuel and by varying the metal nitrate to fuel ratio to understand the role of fuel as well as effect of varying ratio. The experimental result of structural, morphological magnetic and dielectric properties of the prepared samples leads to the following conclusions.

All the samples exhibit single phase formation with cubic structure. The samples prepared by green fuel (black pepper) show better structural properties as compared to inorganic fuel (dextrose). The green synthesis limits the evolution of toxic gases. The sample with 1:1.6 ratio shows better crystallinity and better structural properties.

The infrared spectra of all the samples exhibit two absorption bands indicating the formation of spinel structure. Both fuel and metal nitrate to fuel ratio show influence on the band frequency values and thereby other parameters like force constant.

The morphological studies carried out by FE-SEM indicates that the green fuel show better morphology with minimum particle size.

The magnetic properties such as saturation magnetization, coercivity, remanance magnetization etc are also found to be influenced by varying fuel and varying metal nitrate to fuel ratio. The saturation magnetization increases with increasing metal nitrate to fuel ratio.

The dielectric properties such as dielectric constant, dielectric loss and dielectric loss tangent all show typical decreasing nature with frequency. The values of all these dielectric parameters are also affected by the fuel and metal nitrate to fuel ratio.

Organization of Thesis

The experimental results along with the necessary background of the research work are summarized in the proposed thesis which consists of following chapters.

- **Chapter 1** : Introduction to ferrite
- **Chapter 2** : Synthesis techniques
- **Chapter 3** : Results and discussion on Cd doped cobalt ferrite nanoparticles prepared by (a) dextrose assisted (b) black pepper assisted sol-gel autocombustion synthesis
- **Chapter 4** : Results and Discussion on Cd doped cobalt ferrite nanoparticles prepared by dextrose assisted sol-gel autocombustion synthesis : Effect of metal nitrate to fuel ratio
- **Chapter 5** : Summery/Comparative study and future scope

Rekha Ramrao Parlikar **Prof. K. M. Jadhav**

(Research Student) (Research Guide)

Reference

1. Goldman, A., *Modern ferrite technology*. 2006: Springer Science & Business Media.
2. Ahmed, M.A.A., *A review on the properties and uses of ferrite magnet*. 2017, Sudan University of Science and Technology.
3. Jadhav, V.V., R.S. Mane, and P.V. Shinde, *Basics of Ferrites: Structures and Properties*, in *Bismuth-Ferrite-Based Electrochemical Supercapacitors*. 2020, Springer. p. 37-45.
4. Jadhav, V.V., S.D. Shirsat, U.B. Tumberphale, and R.S. Mane, *Properties of ferrites*, in *Spinel Ferrite Nanostructures for Energy Storage Devices*. 2020, Elsevier. p. 35-50.
5. Tatarchuk, T., M. Bououdina, J. Judith Vijaya, and L. John Kennedy. *Spinel ferrite nanoparticles: synthesis, crystal structure, properties, and perspective applications*. in *International conference on nanotechnology and nanomaterials*. 2016. Springer.
6. Naeem, M., N.A. Shah, I.H. Gul, and A. Maqsood, *Structural, electrical and magnetic characterization of Ni–Mg spinel ferrites.* Journal of Alloys and Compounds, 2009. **487**(1-2): p. 739-743.
7. Amiri, M., M. Salavati-Niasari, and A. Akbari, *Magnetic nanocarriers: evolution of spinel ferrites for medical applications.* Advances in colloid and interface science, 2019. **265**: p. 29-44.
8. Mmelesi, O.K., N. Masunga, A. Kuvarega, T.T. Nkambule, B.B. Mamba, and K.K. Kefeni, *Cobalt ferrite nanoparticles and nanocomposites: Photocatalytic, antimicrobial activity and toxicity in water treatment.* Materials Science in Semiconductor Processing, 2021. **123**: p. 105523.
9. Tundo, P., P. Anastas, D.S. Black, J. Breen, T.J. Collins, S. Memoli, J. Miyamoto, M. Polyakoff, and W. Tumas, *Synthetic pathways and processes in green chemistry. Introductory overview.* Pure and Applied Chemistry, 2000. **72**(7): p. 1207-1228.
10. Bhagwat, V., A.V. Humbe, S. More, and K. Jadhav, *Sol-gel auto combustion synthesis and characterizations of cobalt ferrite nanoparticles: Different fuels approach.* Materials Science and Engineering: B, 2019. **248**: p. 114388.
11. Gole, D.A., S.B. Kapatkar, and S.N. Mathad, *Eco-friendly synthesis of nano-sized cobalt ferrites and influence of pH variation on structural properties.* Inorganic and Nano-Metal Chemistry, 2022: p. 1-9.
12. Vinosha, P.A. and S.J. Das, *Investigation on the role of pH for the structural, optical and magnetic properties of cobalt ferrite nanoparticles and its effect on the photo-fenton activity.* Materials Today: Proceedings, 2018. **5**(2): p. 8662-8671.
13. Rani, B.J., M. Ravina, B. Saravanakumar, G. Ravi, V. Ganesh, S. Ravichandran, and R. Yuvakkumar, *Ferrimagnetism in cobalt ferrite (CoFe2O4) nanoparticles.* Nano-Structures & Nano-Objects, 2018. **14**: p. 84-91.
14. Karakas, İ.H., *The effects of fuel type onto the structural, morphological, magnetic and photocatalytic properties of nanoparticles in the synthesis of cobalt ferrite nanoparticles with microwave assisted combustion method.* Ceramics International, 2021. **47**(4): p. 5597-5609.
15. Vinosha, P.A., A. Manikandan, R. Ragu, A. Dinesh, K. Thanrasu, Y. Slimani, A. Baykal, and B. Xavier, *Impact of nickel substitution on structure, magneto-optical, electrical and acoustical properties of cobalt ferrite nanoparticles.* Journal of Alloys and Compounds, 2021. **857**: p. 157517.
16. Purnama, B. and A.T. Wijayanta, *Effect of calcination temperature on structural and magnetic properties in cobalt ferrite nano particles.* Journal of King Saud University-Science, 2019. **31**(4): p. 956-960.